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**Tetraalkyldiarsines as Precursors in the Synthesis of Electronic Materials:
Synthesis and Characterization of Various *iso*-Propyl Arsenic Compounds**

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TETRAALKYLDIARSINES AS POTENTIAL PRECURSORS FOR ELECTRONIC MATERIALS: SYNTHESIS AND CHARACTERIZATION OF VARIOUS *ISO*-PROPYL ARSENIC COMPOUNDS

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ABSTRACT

Tetrakis(iso-propyl)diarsine was synthesized by the reaction of $(i\text{-Pr})_2\text{AsLi}$ with $(i\text{-Pr})_2\text{AsI}$. The lithium salt of the secondary arsine was produced following deprotonation of $(i\text{-Pr})_2\text{AsH}$, obtained by reduction of $(i\text{-Pr})_2\text{AsI}$, which was prepared by the thermolysis of $(i\text{-Pr})_3\text{AsI}_2$. The X-ray crystal structure of $[(i\text{-Pr})_3\text{AsI}][\text{I}]$ has been determined on the product of the reaction of $(i\text{-Pr})_3\text{As}$ and I_2 . Compounds of the general form $\text{E}=\text{As}(i\text{-Pr})_3$ ($\text{E} = \text{O}, \text{S}, \text{Se}$) have been prepared.

INTRODUCTION

Several recent publications have discussed the potential of utilizing *tetrakis(alkyl)diarsines* as *in situ* sources of arsenic for employment in the preparation of arsenic-containing electronic materials.¹ Such routes to, for example, GaAs presently rely on toxic and highly volatile precursors (*e.g.*, AsH_3). The motivation for this new approach is depicted in equation 1. Although the molecularity of the arsenic-containing product is uncertain, such routes have seen some moderate success. The precise stoichiometry of the reaction product may be $1/2 (\text{As}_4)$ or 2As ; however, the confirmation of this synthetic procedure for *in situ* generation of elemental arsenic-containing species relies less on the accretion coefficient, and more on the lack of any carbon-containing species in the product. Such contamination by the disadvantageous decomposition of pendant organic groups highly is detrimental to the final electronic properties of such materials.

[‡]Deceased 22 December 1992

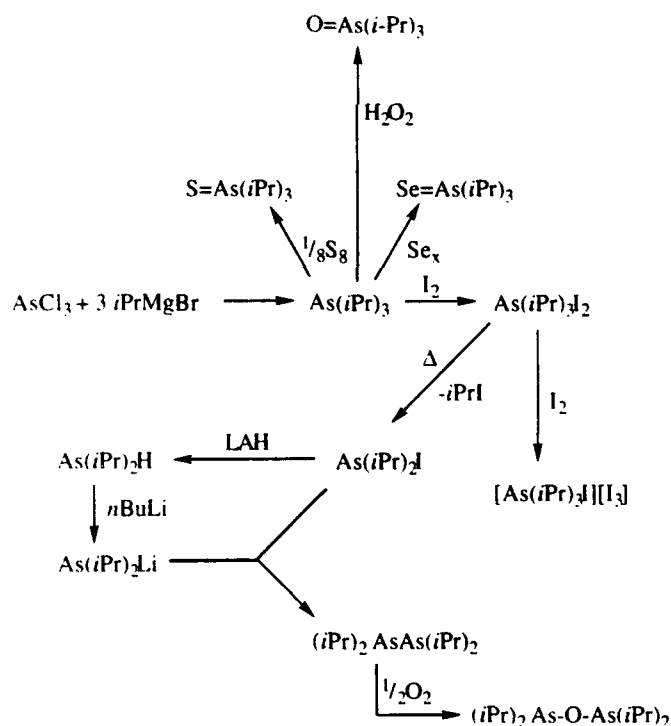
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As one component of a program directed at an examination of the generality of this approach,^{1c} several *iso*-propyl arsenic compounds have been prepared. The synthesis and characterization of some of these organometallic compounds is reported in this contribution.



RESULTS AND DISCUSSION

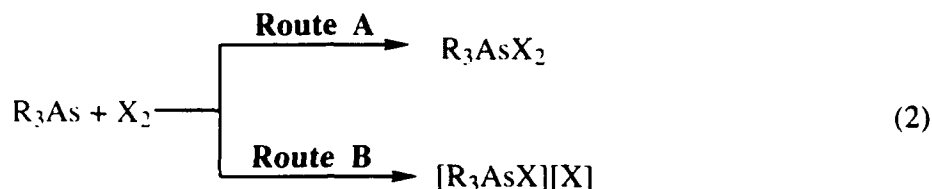
Credit is given to Cadet for the initial report of a compound containing a metal-carbon bond.² His 1760 paper describes the simplest tetraalkyldiarsine, $(\text{H}_3\text{C})_2\text{As-As}(\text{CH}_3)_2$, given the trivial name of cacodyl. A variety of methods have been developed over the years for the preparation of diarsines.³ In order to address the above-described motivation for exploration of tetraalkyldiarsines as potential precursors in the OMVPE growth of high-quality semiconducting materials, *tetrakis(iso-propyl)diarsine* was prepared (Scheme I).



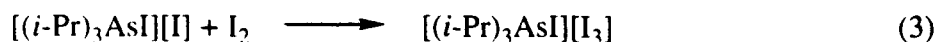
Scheme I

Crystal structures of [(*i*-Pr)₃AsI][I] and [(*i*-Pr)₃AsI][I₃]

The general format for the oxidative addition of a dihalogen molecule to a tertiary organoarsine (equation 2) can proceed according to two alternate pathways.



In Route A, the $\sim T_d$ $R_3\text{As}$ is transformed into the molecular $R_3\text{AsX}_2$ with a trigonal bipyramidal geometry. In Route B, the resultant product is an [arsonium][halide] ionic moiety. Factors influencing the path of choice include the electronic and spatial considerations of the alkyl groups represented in the tertiary arsine, as well as the $\Delta\chi$ present between the halogen and arsenic. For example, both $[\text{Me}_3\text{PX}][\text{X}]$ and Me_3SbX_2 have been characterized.⁴ In all likelihood, the difluorides are covalently bound. Previous infrared spectroscopic work has indicated that $R_3\text{AsI}_2$ compounds ($R = \text{Me}, \text{Et}$) are ionic in the solid state.⁵ In the present investigation, [(*i*-Pr)₃AsI][I] was determined, by X-ray diffraction, to be the conformation adopted by the reaction product of (*i*-Pr)₃As and I₂. If the stoichiometry was not carefully controlled (equation 3), a different product was obtained. There have been reports of comparable reactions observed for Ph_3As .⁶



A single crystal structure determination also was conducted on [(*i*-Pr)₃AsI][I₃]. It was, however, suspended prior to complete refinement. Once the identical atomic linkages were ascertained to be present in the organometallic cation, the structural refinement was not pursued further. There was little new structural information revealed in the anion replacement species.

Pertinent crystal and refinement data along with selected interatomic distances and angles will be published elsewhere. An ORTEP representation of the structure is presented (Figure 1), including both covalent and ionic interactions between As and I atoms.

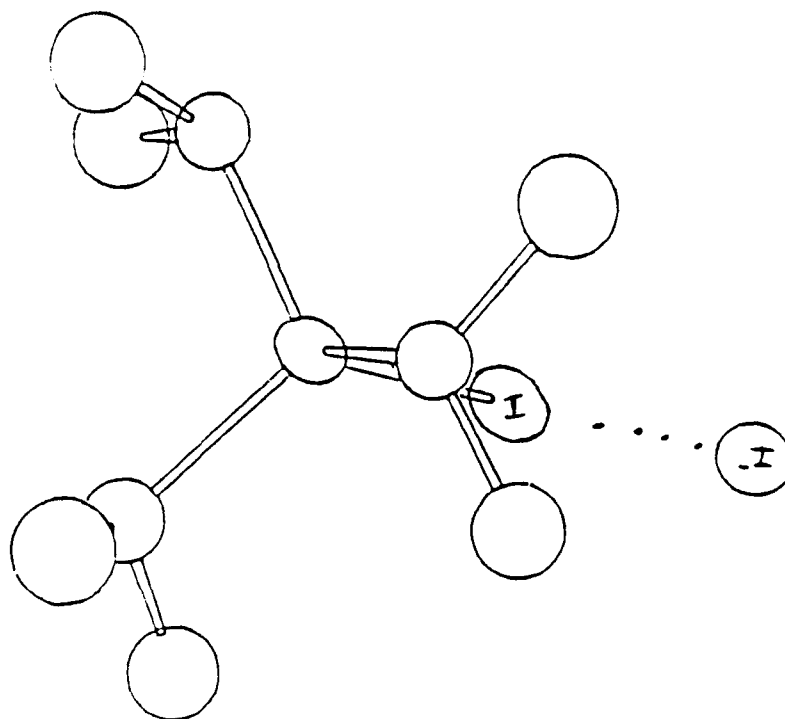
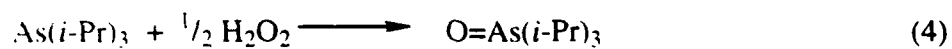


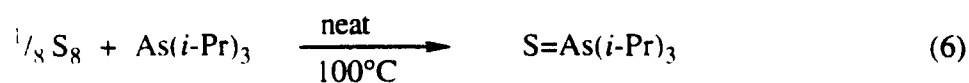
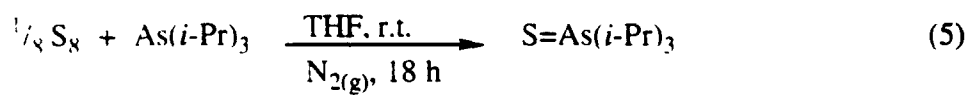
Figure 1 ORTEP representation of $[(i\text{-Pr})_3\text{AsI}][\text{I}]$
Open circles represent Carbon atoms. Hydrogen
atoms have been omitted for clarity of presentation.

Preparation of $\text{E}=\text{As}(i\text{-Pr})_3$ ($\text{E} = \text{O}, \text{S}, \text{Se}$)

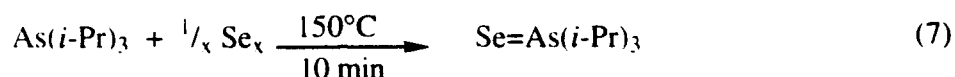
The preparation of $\text{O}=\text{As}(i\text{-Pr})_3$ was effected under mild conditions (equation 4).



Either a solvent-mediated or a direct reaction can be utilized in the synthesis of $\text{S}=\text{As}(i\text{-Pr})_3$ (equation 5 - 6).



The most efficient route for the preparation of $\text{Se}=\text{As}(i\text{-Pr})_3$ was determined to be the reaction of $\text{As}(i\text{-Pr})_3$ with elemental selenium (equation 7).



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